Dredging Research

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Rapid, sediment-specific indicators of hydrophobic organic contaminants bioavailability proposed

By Herbert L. Fredrickson, Ph.D., ERDC Environmental Laboratory, Vicksburg, MS

Approximately 400 million cubic yards of sediments is dredged from U.S. ports, harbors, and waterways each year to maintain the nation's navigation system. Approximately 10 to 20 percent of this material is impacted with organic contaminants. Much of this dredged material is placed in diked confined disposal facilities. The U.S. Army Corps of Engineers would like to recycle this material for beneficial uses, and the Corps is required by the Clean Water Act to assess the potential for these contaminants to accumulate in biota. Simple models based on fugacity (e.g., the organic carbon normalized partitioning coefficient (K_{oc})) have been developed and are widely used to predict the partitioning of hydrophobic organic contaminants (HOC) between organic matter and organism lipid. Commonly used fugacity models assume HOC partitioning behavior is dictated by the amount of organic carbon in sediments and is independent of the quality of this organic matter. However, many publications have shown that the quality of organic carbon can greatly affect the bioavailability of HOC. K_{oc}-based predictions of HOC partitioning behavior were compared to directly measured HOC partitioning to solid phase extraction (SPE) materials using sediments from on-going Corps dredging operations.

Experimental

Sediments from eight current Corps dredging projects were collected and characterized with respect to:

- HOC types and levels,
- Particle size distributions,
- Total organic carbon (TOC),
- Cation exchange capacity,
- Total C, H, N, O, and S,
- Readily desorpable HOC fraction using solid phase extraction materials,
- Black carbon content,
- Microbial biomass and community composition using phospholipid fatty acid analysis,
- Potential rates of HOC biodegradation.

Results

The goal of the study was to determine if simple fugacity models could be used to predict the partitioning behavior of HOC in sediments representative of the range of physico-chemical properties typically found in channels maintained by the Corps. The eight sediments examined exhibited a

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Table 1. Comparison of sediment physical and chemical characteristics

Characteristic	Housatonic	Waukegan	Milwaukee	Kinnic	Calumet	Green Bay	New Bedford	Indiana
Total Carbon %	2.37	5.48	5.75	7.39	4.48	7.10	4.91	10.11
Black Carbon %	0.00	2.85	5.22	7.37	7.91	8.17	9.19	7.84
Total Organic Carbon (%)	1.40	3.80	6.80	9.40	9.60	12.70	14.10	15.70
Clays (%)	4.20	8.20	10.60	11.20	5.40	12.30	7.00	6.40
Sands (%)	40.00	30.20	28.20	24.00	25.80	31.70	28.60	29.40
Silt (%)	55.80	61.60	61.20	64.80	68.80	56.00	64.40	64.20
Cation Exchange Capacity (meq/100 g)	2.30	4.80	12.90	16.40	9.80	30.40	19.60	10.70
pH	6.60	7.50	7.30	7.10	7.50	7.00	6.70	7.00
PAH (polyaromatic hydrocarbons)								
Total solvent-extractable PAH (ng/gdw)	1.17	5.25	49.59	40.59	50.04	1.17	33.51	236.50
Readily Desorbed PAH (%)	7.37	0.62	11.76	40.34	28.81	13.64	15.66	73.32
K_{oc}-predicted PAH partioning (%)	27.30	26.20	24.11	22.30	18.25	20.00	24.94	28.41
K_{oc} with K_{bc}-predicted PAH partioning (%)	25.83	24.76	23.86	23.05	21.09	22.74	24.45	25.72
PCB (polychlorinated biphenyls)								
Total solvent-extractable PCB (ng/gdw)	32.62	5.13	2.88	1.90	5.61	0.67	1559.73	41.43
Readily Desorbed PCB (%)	9.33	18.35	60.12	94.26	49.57	93.49	76.26	70.95
K_{oc}-predicted PCB partioning (%)	52.30	65.35	62.52	60.06	46.17	56.95	64.73	64.25
K_{oc} with K_{bc}-predicted PCB partioning (%)	51.97	55.14	57.96	60.51	75.33	61.48	55.22	54.72

wide range of physicochemical characteristics (Table 1). The columns in Table 1 read from left to right in increasing percentages of TOC because many sediment characteristics are directly related to TOC. The trend of increasing percentages of total carbon (TC), TOC, and black carbon from left to right in Table 1 is also reflected in the trend in the percentages of bulk silt. However, no such trend was seen for the other measured parameters.

Discussion

The levels of total solvent-extractable PAH ranged from 1.17 ng/gram dry weight (gdw) in Housatonic River sediment to 236.5 ng/gdw in Indiana Harbor sediment. As might be expected of sediments taken from systems with different histories of anthropogenic discharges, there was no correlation between total solvent-extractable PAH and TC or TOC. The percentage of total solvent-extractable PAH that partitioned to C_{18} filters in 28 days ranged from 0.62 to 73.32 percent. These percentages were not correlated to the levels of total solvent-extractable PAH in the sediments. More importantly with respect to K_{oc}-based partitioning models, there was also little correlation ($r^2 = 0.42$, increasing trend) between readily desorbed PAH and TOC (Figure 1). Consistent and accurate predictions of HOC partitioning behavior based on K_{oc} as described by Karickhoff (see

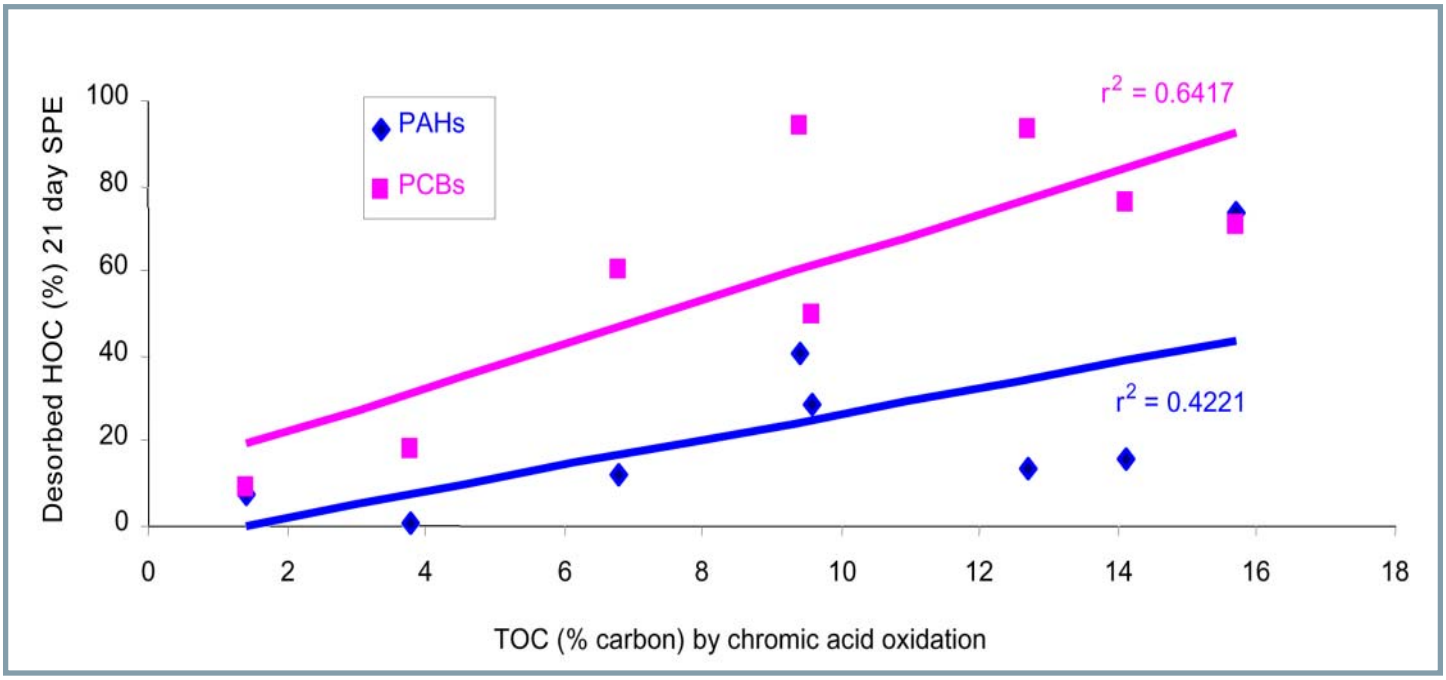
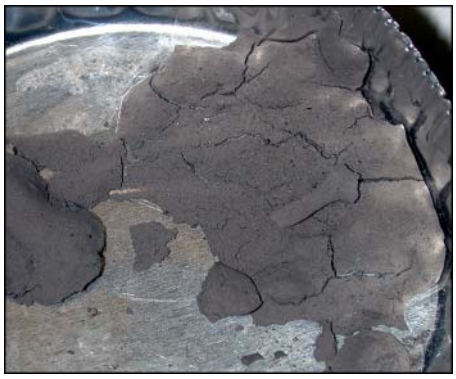


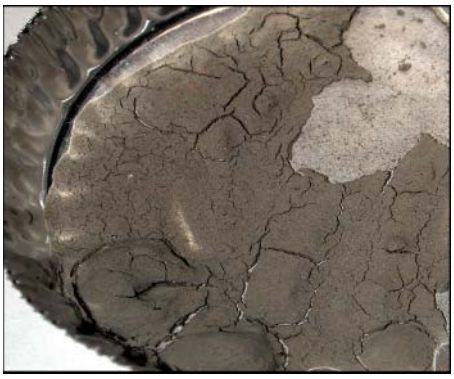
Figure 1. Relationship between percentages of readily desorbed HOC and sediment TOC

Indiana Harbor

New Bedford



Calumet



Kinnic

Waukegan

Housatonic

footnote) are based on the presence of this correlation. K_{oc}-based partitioning predictions ranged around 20 percent for all the sediments. Overestimating the readily desorbed total PAH fraction in five of the sediments, and underestimating partitioning in sediments from Kinnic River, Calumet River, and Indiana Harbor occurred.

The levels of black carbon in the sediments ranged from 0 in Housatonic to 9.19 percent in New Bedford Harbor sediment. The levels of black carbon in the sediments increased with the levels of TOC in the various sediments (that is, from left to right in Table 1) with the exception of New Bedford Harbor. New Bedford Harbor was the only site with saline water. Incorporation of a black carbon term into Karickhoff's K_{oc} HOC partitioning model also resulted in predictions that about 20 percent of the total solvent-extractable PAH would be readily desorbed. Predictions using the black carbon term ranged from 21.09 percent in Calumet sediment to 25.83 percent in Housatonic sediment. Use of the black carbon term did not improve the accuracy of the predictions relative to the total PAH that was sorbed to C_{18} filters (Table 1). It also proved difficult to accurately predict PCB partitioning behavior in these sediments using simple fugacity models. The levels of total solvent-extractable PCB ranged from 0.67 ng/gdw of sediment in Green Bay to 1,560 ng/gdw of sediment in New Bedford Harbor. Although there was a better correlation ($r^2 = 0.64$) between readily desorbed PCB and TOC than seen with readily desorbed PAH, this correlation was not strong (Figure 1).

K_{oc}-based predictions of PCB portioning ranged from 46.17 to 65.35 percent of the total solvent-extractable PCB (Table 1). Three of these percentages were higher than the percentages of readily desorbed PCB (i.e., measured on the C_{18} filters) while five were lower. Inclusion of the black carbon term improved the accuracy of the K_{oc}-based prediction of total PCB partitioning with respect to the readily desorbed total PCB (i.e., 28-day sorption to C_{18} filters) for six of the eight sediments.

Conclusions

The Corps spends over $500 million annually on dredging. The volume of sediment to be managed—together with the propensity for HOC to accumulate in sediments, the heterogeneous distribution of HOC in sediments, and the continual movement of sediments and resorting of particles during transport—results in the practical need for rapid screening procedures.

Simple fugacity-based HOC partitioning models enable sediment managers to:

- Estimate potential bioaccumulation with sediment-specific information on levels of HOC and TOC.

- Look up values of HOC octanol-water partitioning coefficients in published tables.

The facility of this model and its low data demands have resulted in its wide application. However, as Karickhoff has pointed out, "acceptability of a predictor depends upon the use to be made of the resulting number(s), the span of the environmental conditions over which the predictor is to be applied, and the degree of accuracy or precision required in its usage."

Since sediment organic matter is generally a good sorbant of HOC, it can be intuitively expected that the amount of organic matter in sediments would affect HOC partitioning from water to sediment. In terms of partitioning coefficients (K_d), it would be convenient if there would be a linear relationship, namely

$$K_d = f_{oc} \times K_{oc}$$

where f_{oc} is the fraction of organic carbon. The value of f_{oc} is measured, but K_{oc} is unknown for a given sample. For most organic carbon, K_{oc} is related to K_{ow}, the octanol-water partitioning coefficient tabulated for each compound. Tables of K_{ow} have been published. For a mixture of compounds, such as total PCB or total PAH, an average K_{ow} and the average K_{oc} must be calculated. The resulting distribution coefficient K_d is then a measure of the total HOC partitioning between water and sediment.

However, in the data presented here, there is a lack of correlation between the quantity of organic carbon and the readily desorbable fraction of PAHs and PCBs in these sediments. If there were simple partitioning into the organic carbon (i.e. any K_{oc} model, including nonlinear models), then the ratio of desorbable PCBs to desorbable PAHs should be constant. This fundamental result is not observed (Figure 2), and the obvious reason is that not all organic carbon is the same. When the ratio of desorbable PCBs to desorbable PAHs is not constant, there is a variable bias. For most of these sediments, the PCBs are more readily desorbable than the PAHs. This bias factor ranges from a high of 30 for the Waukegan sediment, with roughly equal total extractable PAHs and PCBs, to a low of 1 for the Indiana sediment. This variable bias could come from several sources. One is the potentially variable absorption and desorption of different HOCs for the SPE procedure, despite the use of recovery standards. For spiked compounds the recovery was essentially 100 percent for all our analyses. Another source of variability could be the use of the lumped parameters total PAHs and total PCBs. However, for many of the sediments the individual PCBs and PAHs were similar if not identical, and yet they still had bias in the recovery ratio. This narrowing of the potential sources of variability leaves the sediment itself and, probably, the quality of the organic carbon in these sediments.

Some of the recent literature has focused on black carbon. We used a black carbon normalized partitioning coefficient (K_{bc}) and the fraction of black carbon in the sediment (f_{bc}) in an attempt to improve the accuracy of fugacity-based predictions.

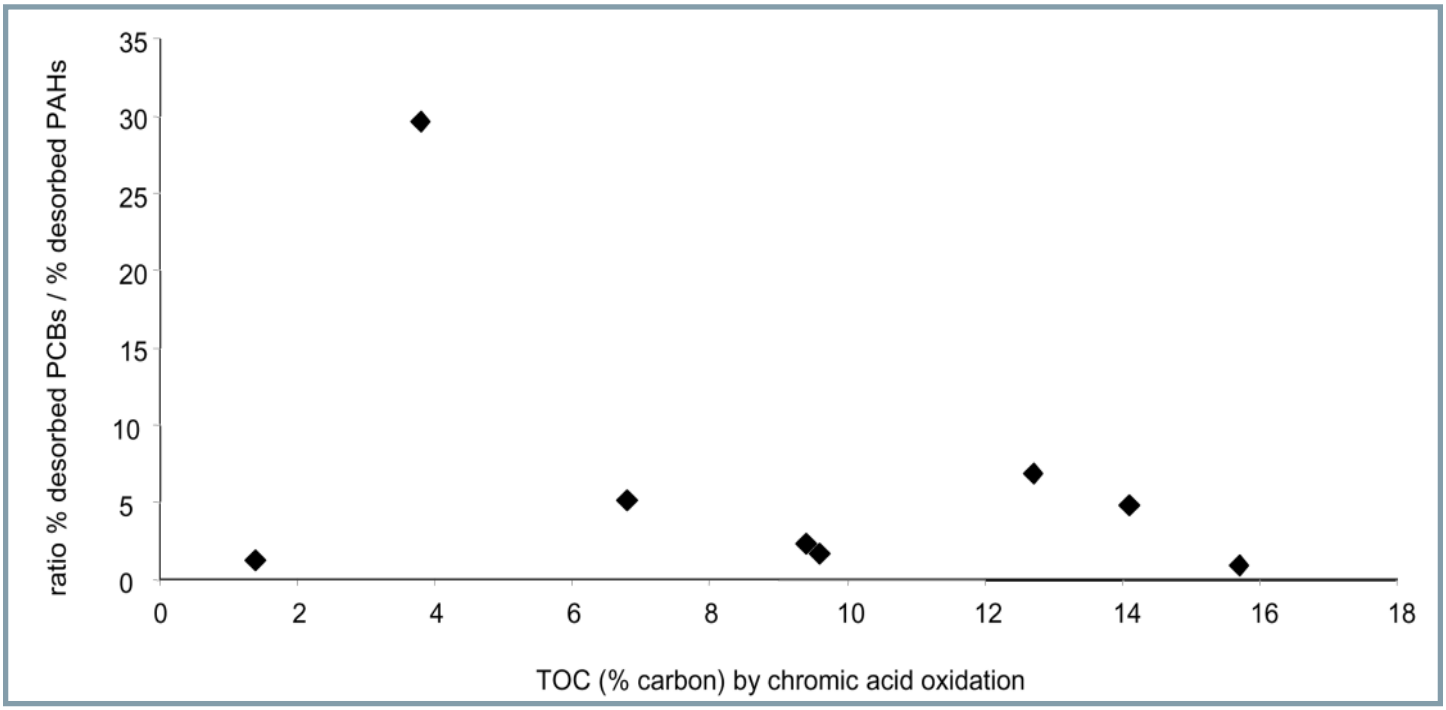


Figure 2. Relationship between ratio of readily desorbed PCB to PAH and sediment TOC

$$K_d = f_{oc} \times K_{oc} + f_{bc} \times K_{bc}$$

However, similar results were obtained. Thus, neither the linear organic carbon partitioning nor the extended linear organic carbon + black carbon models consistently explained HOC sorption onto C_{18} filters from the sediments in our experiments.

Using a reference sediment with physical and chemical characteristics similar to the one being evaluated can improve the accuracy of K_{oc}-based partitioning predictions. The uncertainty of K_{oc}-based HOC partitioning has been discussed.

Summary

HOC-contaminated sediments were opportunistically chosen from ongoing dredging studies. The physical and chemical properties of these sediments varied widely. Simple fugacity models based on K_{oc} and K_{oc} with a black carbon term failed to accurately or consistently predict the total levels of PAH or PCB that were readily desorbed. Use of a functionally defined, readily desorbed HOC fraction is a rapid means of obtaining sediment-specific information on the bioavailability of HOC. Additional work is required to relate readily desorbed HOC to body burdens in benthic infauna.

Karickhoff, S.W. (1981). "Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils," *Chemosphere* 10:833-846.

More information is available from Herbert L. Fredrickson, ERDC Environmental Laboratory. Publications include American Chemical Society, 225th National Meeting New Orleans, LA, 23-27, *Bioavailability of hydrophobic organic contaminants and quality of organic carbon.* March 2003, Vol. 43 No. 1. Technical Note ERDC/TN EEDP-01-50, *"Development of a new bioaccumulation testing approach: The use of DDE as a challenge chemical to predict contaminant bioaccumulation,"* May 2003, can be found at *http://www. wes.army.mil/el/dots/eedptn.html*.

Dredging Research editor farewell and thanks to readers, contributors, and publishers

After 6 years as editor for the *Dredging Research* Information Exchange Bulletin, it is time to say good-bye. It has been a wonderful success story, and an interesting and informative journey, to bring U.S. Army Corps of Engineers dredging research-related information to more than 3,000 subscribers worldwide.

In our transition to an electronic version, the subscriber base to the listserver has grown to approximately 1,500, while the mailing list for the printed bulletin is still strong at more than 2,000 subscriptions. The interest expressed by our readership attests to the timeliness of information presented in the publication.

The bulletin could not have had the quality of contents without the support from Corps dredging research managers and all the contributors. Articles in the issues of *Dredging Research* came from many sources and that fact added diversity to the contents. To all of you who supported the bulletin, my heartfelt thanks. You have been immensely patient with me and the deadlines we have met so faithfully for the past 6 years.

Finally, my thanks to Jamie Leach, Betty Watson, and Angie Jackson who are part of the in-house publishing staff for the bulletin and were instrumental in the fine products that were presented to our readers.

Many thanks to all of you,
Elke Briuer, APR, MSComm.

Dredging Calendar

2003

October 1–Title and abstract due for WODCON XVII. See more information under 2004. Call for Papers, *http://www.woda.org/WODCONXVII/pages/WodconXVII-CFP.pdf* (pdf - 704 kb).

October 1-2–WEDA Midwest Chapter meeting. Embassy Suites Hotel, St. Louis, Missouri. Theme is Environmental and Beneficial Use of Dredged Material. Contact Don Seibert, chapter president, 812-868-7008; *dseibert@southwindco.com*

October 14-15–WEDA Gulf Chapter meeting, Jefferson Orleans South, Metairie, Louisiana. Contact Charles Settoon, 504-889-0182; *debset99@cox.net*.

November 12-14– WEDA Pacific Chapter meeting, Marriott Waikiki Hotel, Hawaii. Contact chapter president Christine Boudreau, 510-663-4235; *cboudreau@anchorenv.com*.

November 18-21–CARIS 2003, "Gateways in Geomatics," annual user's conference at the Adams Mark Hotel, St. Louis, Missouri. Contact: Sheri Flanagan, CARIS, 264 Rookwood Avenue, Fredericton, New Brunswick, Canada, E3B 2M2. Phone: 506-458-8533; fax: 506-459-3849; *caris2003@caris.com; www.caris.com*.

November 9-13–SETAC 24th Annual Meeting in North America. Science Without Borders: Developing Solutions for Global Environmental Challenges. Austin Convention Center, Austin, Texas. More information can be found at *http://www.setac.org/austinmain.html*.

November 18-22–CEDA Dredging Days and Europort 2003, Amsterdam RAI. 31st International Maritime Exhibition and 13th International Inland Shipping Exhibition. Contact Dr. Anna Csiti, CEDA Secretariat, PO Box 488, 2600 AL Delft, The Netherlands; phone +31-15-2783145; fax: +31-15-2787104. For Europort: Amsterdam RAI, PO Box 77777, 1070 MS Amsterdam, The Netherlands; phone +31-20-549-12-12; *http://show-info.nl/europort2003*

2004

January 11-15–83rd TRB Annual Meeting, Washington, DC, USA.

March 15-18–CONEXPO/CON-AGG. Construction Exposition and Concrete and Aggregate Producers Convention, Las Vegas, Nevada. Contact the National Stone, Sand and Gravel Association (NSSGA) , 2101 Wilson Blvd., Suite 100, Arlington, VA 22201; phone: 800 -342-1415; 703-525-8788; fax: 703-525-7782; *info@nssga.org* or visit *http://www.nssga.org*.

May 23-26–Ports 2004. Port Development in the Changing World, Westin Galleria & Westin Oakes, Houston, Texas. Sponsored by American Society of Civil Engineers and PIANC, and co-hosted by the Port of Houston Authority. Contact ASCE Conferences Department, 1801 Alexander Bell Drive, Reston, VA 20191; phone 703-295-6030; fax: 703-295-6144; *conf@asce.org* or visit *www.asce.org/conferences/ports2004*.

September 27- October 1–WODCON XVII, Dredging in a Sensitive Environment, World Dredging Congress XVII at CCH – Congresss Centrum Hamburg, Germany. In conjunction with SMM 2004, the Shipbuilding, Machinery and Marine Technology International trade fair. Contact the Central Dredging Association, PO Box 488, 2600 AL Delft, The Netherlands.; phone +31 15 278 3145; fax: +31 15 278 7104; *ceda@dredging.org*. More information can be found at *http://www.woda.org/WODCONXVII/index.html*

September 27-October 1–Hamburg, Germany. Invitation to Post Congress Tour (pdf - 232 kb). POC: Anna Caiti, P.O. Box 488 2600 AL Delft, The Netherlands, *ceda@dredging.org*. More information can be found at *www.woda.org* click on "congresses."

Articles for *Dredging Research* requested:

***Dredging Research* is an information exchange bulletin for publication of ERDC-generated dredging research results. Included are articles about applied research projects. The bulletin serves all audiences and is accessible on the World Wide Web in addition to a paper circulation of 2,800.**

Articles from non-ERDC authors are solicited for publication, especially if the work described is tied to the use of ERDC-generated research results. Research articles that complement ERDC research or cover wide field applications are also accepted for consideration. Manuscripts should use a nontechnical writing style and should include suggestions for visuals and an author point of contact. Point of contact is Robert M. Engler, at *Robert.M.Engler@erdc.usace.army.mil*.

September 2003, Deadline February 28, 2004: Call for Papers: Coasts and Ports Australasian Conference, The Hyatt Hotel, Auckland, New Zealand

Consider participating in the 16th Australasian Coastal & Ocean Engineering Conference and 9th Australasian Port & Harbour Conference. The theme of the conference is "Coastal Development - A Quest for Excellence" and the issues it covers include models for "good" coastal development, change in port infrastructure and efficiency, costs of regulation and compliance, managing conservation and development, assessing impacts of coastal structures on the natural system, and changes in science and technology in modeling and monitoring coastal change. Papers on these and other coast and port issues are welcomed. Abstracts should be a maximum of 250 words and should be submitted by February 28, 2004. Electronic submission is preferred and should be sent to: coasts and *ports@tcc.co.nz* both as an attachment and in the body of the email. Postal submissions should be on disk labeled with your name and contact details and sent to the Conference Managers (see below). For submissions and more information, contact:

The Conference Managers
The Conference Company
PO Box 90040, Auckland, New Zealand
telephone: +64 9 360 1240; fax: +64 9 360 1242
email: coasts and *ports@tcc.co.nz*

20 November 2003, CEDA 25th Anniversary Reunion Reception

Dear Readers,

It may have come to your notice that CEDA is preparing for a big celebration this November to coincide with the Dredging Days at Europoort. Why? Because it is our Silver Anniversary.

CEDA is also, and always has been, a talking shop, where friends with a common interest may meet and swap experiences, stories, and anecdotes. So we are going to have a mega talking shop on the evening of 20 November 2003 at the Rai Congress Centre in Amsterdam. We're calling it the CEDA 25th ANNIVERSARY REUNION RECEPTION and it will be a free event, held between 17.30 and 19.30 hr, where you and your partner can enjoy convivial refreshments and a trip down memory lane with your friends and colleagues. There will also be some entertainment and displays for your enjoyment.

The Reception is open to all past and present Members of CEDA, current Members of EADA and WEDA, and those attending the Dredging Days. So, send off for your invitation card (CEDA Secretariat, P.O. Box 488, 2600 AL Delft, The Netherlands. Tel: +31 (0)15 278 3145 Fax: +31 (0)15 278 7104. E-mail: *ceda@dredging.org*) and come and join us in our Silver Celebrations!

Dipl.-Ing Rewert Wurpts
President of CEDA Eur.Ing.

Nick Bray
Chairman of 25th Anniversary Committee

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Dredging Research

This bulletin is published in accordance with AR 25-30 as an information dissemination function of the Environmental Laboratory of the U.S. Army Engineer Research and Development Center. The publication is part of the technology transfer mission of the Dredging Operations Technical Support (DOTS) Program and includes information about various dredging research areas. Special emphasis will be placed on articles relating to application of research results or technology to specific project needs. The contents of this bulletin are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or the approval of the use of such commercial products. Contributions are solicited from all sources and will be considered for publication. Editor is Elke Briuer, APR, *Elke.Briuer@erdc.usace.army.mil*. Mail correspondence to the Environmental Laboratory, ATTN: DOTS, Dredging Research, U.S. Army Engineer Research and Development Center, Waterways Experiment Station (CEERD-EM-D), 3909 Halls Ferry Road, Vicksburg, MS 39180-6199, or call (601) 634-2349. Internet address: *www.wes.army.mil/el/dots/drieb.html*.

James R. Houston, PhD
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DEPARTMENT OF THE ARMY
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